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### (54) Manganese dioxide for lithium primary battery and process for producing the same

Mangandioxid für primäre Lithiumbatterie und Verfahren zu seiner Herstellung

Dioxide de manganèse pour accumulateur primaire au lithium et procédé pour son élaboration

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**Description****BACKGROUND OF THE INVENTION**

## 5 Field of the Invention:

**[0001]** The present invention relates to lithium primary batteries containing manganese dioxide and a process for producing the same. More particularly, it relates to an improvement in a cathode active material of a lithium primary battery comprising lithium or a lithium alloy as an anode active material.

## 10 Description of the Related Art:

**[0002]** Typical cathode active materials known for lithium primary batteries comprising lithium or a lithium alloy as an anode active material include manganese dioxide, carbon fluoride, etc., which have been put to practical use.

**[0003]** Manganese dioxide out of these cathode active materials has been used out of preference because of its inexpensiveness and abundance.

**[0004]** Where manganese dioxide is used as a cathode active material, it is a generally followed practice that electrolytic manganese dioxide is heat treated at 350 to 430°C as disclosed, e.g., in Japanese Patent Publication No. 4064/82.

**[0005]** The electrolytic manganese dioxide to be heat treated is one having been neutralized with ammonia. Electrolytic manganese dioxide itself is useful as a cathode material in manganese dry batteries and alkaline manganese dry batteries. Ammonia-neutralized manganese dioxide is for manganese dry batteries, and soda-neutralized manganese dioxide is for alkaline manganese dry batteries. Electrolytic manganese dioxide having been neutralized with soda and heat treated contains 0.3 to 0.5% by weight of sodium. If the sodium-containing manganese dioxide is applied to a lithium primary battery, the lithium primary battery has significantly reduced discharge performance because the residual sodium in manganese dioxide contaminates the anode lithium to interfere with the electrode reaction, evaporates together with the water content during heat treatment. It has been pointed out, however, that ammonia neutralization is accompanied by the problem of irritating smell given off on ammonia evaporation which deteriorates the working environment. In addition, an existing plant having no step of ammonia neutralization could not be applied as such to preparation of manganese dioxide for lithium primary batteries.

**[0006]** Ammonia-neutralized manganese dioxide has another disadvantage that it undergoes marked reduction in BET specific surface area, which leads to deterioration of low-temperature characteristics or storage characteristics when applied to lithium primary batteries.

35 **SUMMARY OF THE INVENTION**

**[0007]** The present invention has been made in the light of the above-described circumstances. As a result of extensive investigation, the present inventors have found that neutralization of electrolytic manganese dioxide using a sodium-containing neutralizing agent can be accomplished while controlling the sodium content within a given range.

**[0008]** The present invention has been completed based on this finding. The present invention provides a lithium primary battery comprising manganese dioxide as a cathode active material, said manganese dioxide obtainable by neutralization by means of a sodium-containing neutralizing agent and heat treatment of electrolytic manganese dioxide and which has a sodium content of 0.05 to 0.2% by weight.

**[0009]** The present invention also provides a method of manufacturing a lithium primary battery comprising manganese dioxide as a cathode active material comprising the steps of neutralising electrolytic manganese dioxide having sodium content of 0.05 to 0.2% by weight, by means of a sodium-containing neutralising agent and heating the neutralized manganese dioxide.

**[0010]** The lithium primary batteries according to the present invention can bring about improvements in the working environment, can have reduced sodium dissolution, and can bring about improved low-temperature characteristics and storage characteristics of batteries.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**[0011]** The present invention will be more particularly described with reference to the accompanying drawings, in which:

Fig. 1 is a graph of JIS-pH vs. Na content of manganese dioxide;  
 Fig. 2 is a graph of electrical conductivity vs. Na content of manganese dioxide;

Fig. 3 is a graph of dissolved Na vs. Na content of manganese dioxide; and  
 - Fig. 4 is a graph of dissolved SO<sub>4</sub> vs. Na content of manganese dioxide.

#### DETAILED DESCRIPTION OF THE INVENTION

5 [0012] The manganese dioxide for use in lithium primary batteries according to the present invention is electrolytic manganese dioxide obtained by an electrolysis process. As stated above, electrolytic manganese dioxide has advantages of inexpensiveness and abundance.

10 [0013] The electrolytic manganese dioxide for use in the present invention has a sodium content of 0.05 to 0.2% by weight. When used as a cathode active material of a lithium primary battery, electrolytic manganese dioxide having a sodium content exceeding 0.2% by weight has its sodium content displaced with lithium and precipitated to reduce the storage characteristics of the battery. Electrolytic manganese dioxide with a sodium content smaller than 0.05% by weight has residual acidity due to insufficient neutralization, causing reduction in storage characteristics of the battery.

15 [0014] The manganese dioxide for use in the invention preferably has an amount of sodium dissolution of 20 g/l or less. If the amount of sodium dissolution exceeds 20 g/l, sodium will be displaced with lithium to reduce the storage characteristics of the battery as mentioned above.

20 [0015] As compared with ammonia-neutralized manganese dioxide, the soda-neutralized manganese dioxide for use in the present invention is advantageous in that the reduction in BET specific surface area is small when heat treated. That is, when treated at 430°C for 4 hours, ammonia-neutralized manganese dioxide reduces its BET specific surface area from 50 m<sup>2</sup>/g to 20 m<sup>2</sup>/g, while the BET specific surface area of the soda-neutralized manganese dioxide (50 m<sup>2</sup>/g) is not reduced to less than 30 m<sup>2</sup>/g. This means that soda-neutralized manganese dioxide could be heat treated at higher temperatures than ammonia-neutralized manganese dioxide, with the resultant reduction in BET specific surface area being the same, to bring about improvements on low-temperature characteristics and storage characteristics of batteries.

25 [0016] The manganese dioxide for use in the present invention can preferably be produced as follows. The starting manganese dioxide is obtained by electrolysis. For example, a manganese sulfate aqueous solution having a prescribed concentration is electrolyzed at a constant current density while warming by using a carbon plate as a cathode and a titanium plate as an anode to deposit electrolytic manganese dioxide on the anode. The deposited electrolytic manganese dioxide is peeled from the anode, ground, and neutralized. It is particularly preferred to use manganese dioxide having a phosphorus content of 0.05 to 2.0% by weight disclosed in Japanese Patent Publication No. 1698/94.

30 [0017] Neutralization is preferably carried out with a sodium hydroxide aqueous solution. The sodium content in the manganese dioxide may be controlled by using an aqueous solution containing 2.0 to 5.0 g of sodium hydroxide per kg of the manganese dioxide. The sodium hydroxide aqueous solution usually has a concentration of 100 to 150 g/l. The neutralizing agent which can be used is not limited to sodium hydroxide and includes sodium carbonate and sodium hydrogencarbonate having an equivalent sodium content.

35 [0018] The soda-neutralized electrolytic manganese dioxide is washed with water, dried, and then heat treated to obtain manganese dioxide for lithium primary batteries which contains 0.05 to 0.2% by weight of sodium.

40 [0019] The present invention will now be illustrated in greater detail with reference to Examples. The following Examples are presented as being exemplary of the present invention and should not be considered as limiting. Unless otherwise noted, all the percents are by weight.

#### EXAMPLES 1 AND 2 AND COMPARATIVE EXAMPLES 1 TO 3

45 [0020] Electrolytic manganese dioxide having a phosphorus content of 0.25% was neutralized by addition of a sodium hydroxide aqueous solution having the concentration shown in Table 1 below. The neutralized manganese dioxide was collected by filtration, washed with water, and dried. The manganese dioxide was then heated at 430°C for 4 hours. The sodium content of the resulting manganese dioxide is shown in Table 1.

[0021] For comparison, ammonia-neutralized manganese dioxide was prepared in a conventional manner.

50 [0022] A CR123A type battery was assembled with each of the resulting manganese dioxide species as a cathode active material, a solution of LiCF<sub>3</sub>SO<sub>3</sub> in a 1:1 mixed solvent of propylene carbonate and 1,2-dimethoxyethane as an electrolytic solution, and a lithium electrode as an anode material.

[0023] The batteries were subjected to a discharge cycle test in which a 3-second discharge at 900 mA followed by a 27-second rest made one cycle, and the discharge characteristics of the batteries and the color change of the lithium anode are shown in Table 1.

55 [0024] The soda-neutralized manganese dioxide species of Examples 1 and 2 and Comparative Example 1 were further evaluated in terms of JIS-pH, electrical conductivity, Na dissolution, and SO<sub>4</sub> dissolution in accordance with the following method. The results obtained are shown in Table 1.

(1) JIS-pH

Measured in accordance with JIS K1467.

(2) Electrical conductivity

With the use of a supernatant liquid obtained from the mixture of 10 g of manganese dioxide and 200 mL of deionized water after stirring the mixture for 20 minutes, measurement was carried out with a commercially available portable conductivity meter.

(3) Na dissolution

Measured by ICP analysis.

(4) SO<sub>4</sub> dissolution

Measured by ICP analysis.

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TABLE 1

	NaOH (g/kg-MnO <sub>2</sub> )	Na Content (%)	Discharge Cycle	Color Change of Li	Smell on Heat Treatment	Product Na Content (%)	JIS-pH	Conductivity ( $\mu$ Si/cm)	Na Dissolution (mg/l)	SO <sub>4</sub> Dissolution (mg/l)
Example 1	3.0	0.1	101	no change	no smell	0.1	2.4	100	10	35
Example 2	5.0	0.2	100	no change	no smell	0.2	3.4	50	12	12
Comparative Example 1	10.0	0.5	54	observed	no smell	0.5	4.8	150	2.5	8
Comparative Example 2	-	0.01	46	no change	no smell	-	-	-	-	-
Comparative Example 3	NH <sub>3</sub> - neutralized Product	<0.01	100	no change	emitted	-	-	-	-	-

\* The number of cycles of the NH<sub>3</sub>-neutralized product was taken as a standard (100).

5 [0025] It can be seen from Table 1 that the products of Examples 1 and 2 are equal in performance to the conventional product of Comparative Example 3. The conventional soda-neutralized product of Comparative Example 1 and the non-neutralized product of Comparative Example 2 are inferior in cycle characteristics. The conventional ammonia-neutralized product of Comparative Example 3 emitted the smell of ammonia while heat treated. The soda-neutralized products of Examples 1 and 2 have a smaller amount of Na dissolution than the product of Comparative Example 1.

## TEST EXAMPLE

10 [0026] Manganese dioxide species having a varied sodium content were prepared in the same manner as described above. The influence of the sodium content on JIS-pH, conductivity, Na dissolution, and SO<sub>4</sub> dissolution are shown in the plots in Figs. 1 through 4. It is recognized from these plots that the JIS-pH and Na dissolution reduce and the SO<sub>4</sub> dissolution increases with a decrease of the Na content.

## 15 Claims

1. A lithium primary battery comprising manganese dioxide as a cathode active material, said manganese dioxide obtainable by neutralization by means of a sodium-containing neutralizing agent and heat treatment of electrolytic manganese dioxide and which has a sodium content of 0.05 to 0.2% by weight.
- 20 2. A lithium primary battery according to claim 1, wherein the electrolytic manganese dioxide has a phosphorus content of 0.05 to 2.0% by weight.
- 25 3. A lithium primary battery according to claims 1 or 2, wherein the neutralizing agent is an aqueous solution containing 2.0 to 5.0g of sodium hydroxide, or a sodium content equivalent thereto, per kg of manganese dioxide.
4. A lithium primary battery according to claims 1, 2 or 3, wherein the neutralizing agent is an aqueous solution of one or more of sodium hydroxide, sodium carbonate and sodium hydrogencarbonate.
- 30 5. A method of manufacturing a lithium primary battery comprising manganese dioxide as a cathode active material comprising the steps of neutralising electrolytic manganese dioxide having sodium content of 0.05 to 0.2% by weight, by means of a sodium-containing neutralising agent and heating the neutralised manganese dioxide.
- 35 6. A method according to claim 5, wherein the electrolytic manganese dioxide has a phosphorous content of 0.05 to 2.0% by weight.
7. A method according to claims 5 or 6, wherein the neutralising agent is in an aqueous solution containing 2.0 to 5.0 g of sodium hydroxide, or a sodium content equivalent thereto, per Kg of manganese dioxide.
- 40 8. A method according to claims 5, 6 or 7, wherein the neutralising agent is an aqueous solution of one or more of sodium hydroxide, sodium carbonate and sodium hydrogencarbonate.

## Patentansprüche

- 45 1. Lithiumprimärbatterie mit Mangandioxid als ein kathodenaktives Material, wobei das Mangandioxid durch Neutralisation mittels eines natriumhaltigen Neutralisationsreagenzes und Hitzebehandlung von elektrolytischem Mangandioxid erhältlich ist und welches einen Natriumgehalt von 0,05 bis 0,2 Gewichtsprozent aufweist.
- 50 2. Lithiumprimärbatterie nach Anspruch 1, worin das elektrolytische Mangandioxid einen Phosphorgehalt von 0,05 bis 0,2 Gewichtsprozent aufweist.
3. Lithiumprimärbatterie nach Anspruch 1 oder 2, worin das Neutralisationsreagenz eine wässrige Lösung ist, die 2,0 bis 5,0g Natriumhydroxid oder eine hierzu äquivalenten Natriumgehalt pro kg Mangandioxid enthält.
- 55 4. Lithiumprimärbatterie nach Anspruch 1, 2 oder 3, worin das Neutralisationsreagenz eine wässrige Lösung von einem Natriumhydroxid, Natriumcarbonat Natriumhydrogencarbonat oder einer Kombination hiervon ist.

5. Verfahren zum Herstellen einer Lithiumprimärbatterie mit Mangandioxid als ein kathodenaktives Material, das die Schritte zum Neutralisieren von elektrolytischem Mangandioxid, das einen Natriumgehalt von 0,05 bis 2 Gewichtsprozent aufweist und Erhitzen des neutralisierten Mangandioxids umfasst.
- 5 6. Verfahren nach Anspruch 5, worin das elektrolytische Mangandioxid einen Phosphorgehalt von 0,05 bis 0,2 Gewichtsprozent aufweist.
- 10 7. Verfahren nach Anspruch 5 oder 6, worin das Neutralisationsreagenz eine wässrige Lösung ist, die 2,0 bis 5,0 g Natriumhydroxid oder eine hierzu äquivalenten Natriumgehalt pro kg Mangandioxid enthält.
- 15 8. Verfahren nach Anspruch 5, 6 oder 7, worin das Neutralisationsreagenz eine wässrige Lösung von einem Natriumhydroxid, Natriumcarbonat, Natriumhydrogencarbonat oder einer Kombination hiervon ist.

15 **Revendications**

1. Accumulateur primaire au lithium, comprenant du dioxyde de manganèse en tant que matériau actif de cathode, ledit dioxyde de manganèse pouvant être obtenu par neutralisation au moyen d'un agent de neutralisation contenant du sodium, et par traitement thermique de dioxyde de manganèse électrolytique, et qui a une teneur en sodium de 0,05 à 0,2 % en poids.
2. Accumulateur primaire au lithium selon la revendication 1, dans lequel le dioxyde de manganèse électrolytique a une teneur en phosphore de 0,05 à 2,0 % en poids.
- 25 3. Accumulateur primaire au lithium selon la revendication 1 ou 2, dans lequel l'agent de neutralisation est une solution aqueuse contenant 2,0 à 5,0 g d'hydroxyde de sodium, ou une teneur en sodium équivalente à celle-ci, par kg de dioxyde de manganèse.
- 30 4. Accumulateur primaire au lithium selon la revendication 1, 2 ou 3, dans lequel l'agent de neutralisation est une solution aqueuse d'un ou de plusieurs éléments parmi l'hydroxyde de sodium, le carbonate de sodium et l'hydrogénocarbonate de sodium.
- 35 5. Procédé de fabrication d'un accumulateur primaire au lithium comprenant du dioxyde de manganèse en tant que matériau actif de cathode, comprenant les étapes de neutralisation du dioxyde de manganèse électrolytique ayant une teneur en sodium de 0,05 à 0,2 % en poids, au moyen d'un agent de neutralisation contenant du sodium, et de chauffage du dioxyde de manganèse neutralisé.
- 40 6. Procédé selon la revendication 5, dans lequel le dioxyde de manganèse électrolytique a une teneur en phosphore de 0,05 à 2,0 % en poids.
7. Procédé selon la revendication 5 ou 6, dans lequel l'agent de neutralisation est dans une solution aqueuse contenant 2,0 à 5,0 g d'hydroxyde de sodium, ou une teneur en sodium équivalente à celle-ci, par kg de dioxyde de manganèse.
- 45 8. Procédé selon la revendication 5, 6 ou 7, dans lequel l'agent de neutralisation est une solution aqueuse d'un ou de plusieurs éléments parmi l'hydroxyde de sodium, le carbonate de sodium et l'hydrogénocarbonate de sodium.

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Fig. 1

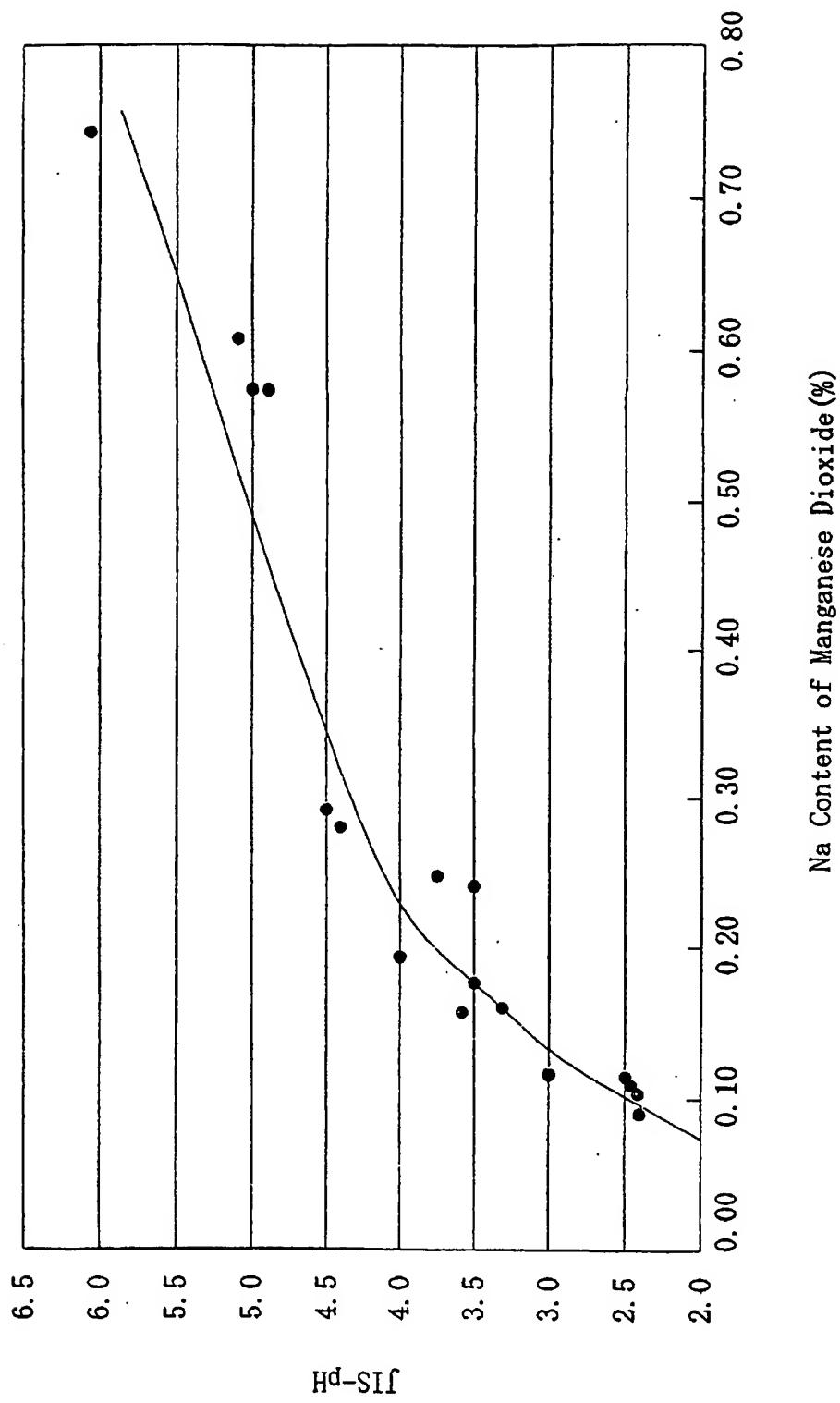


Fig. 2

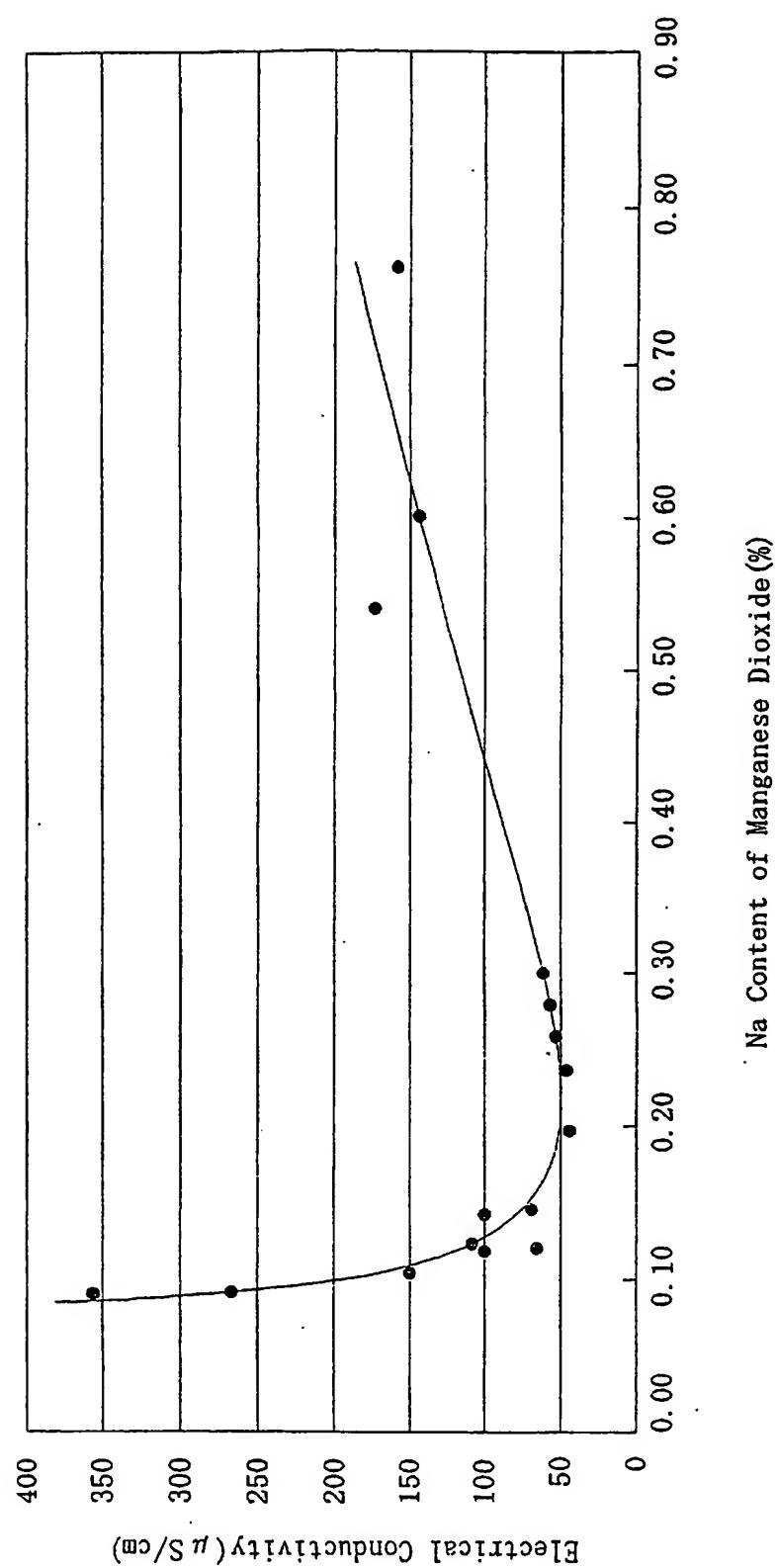


Fig. 3

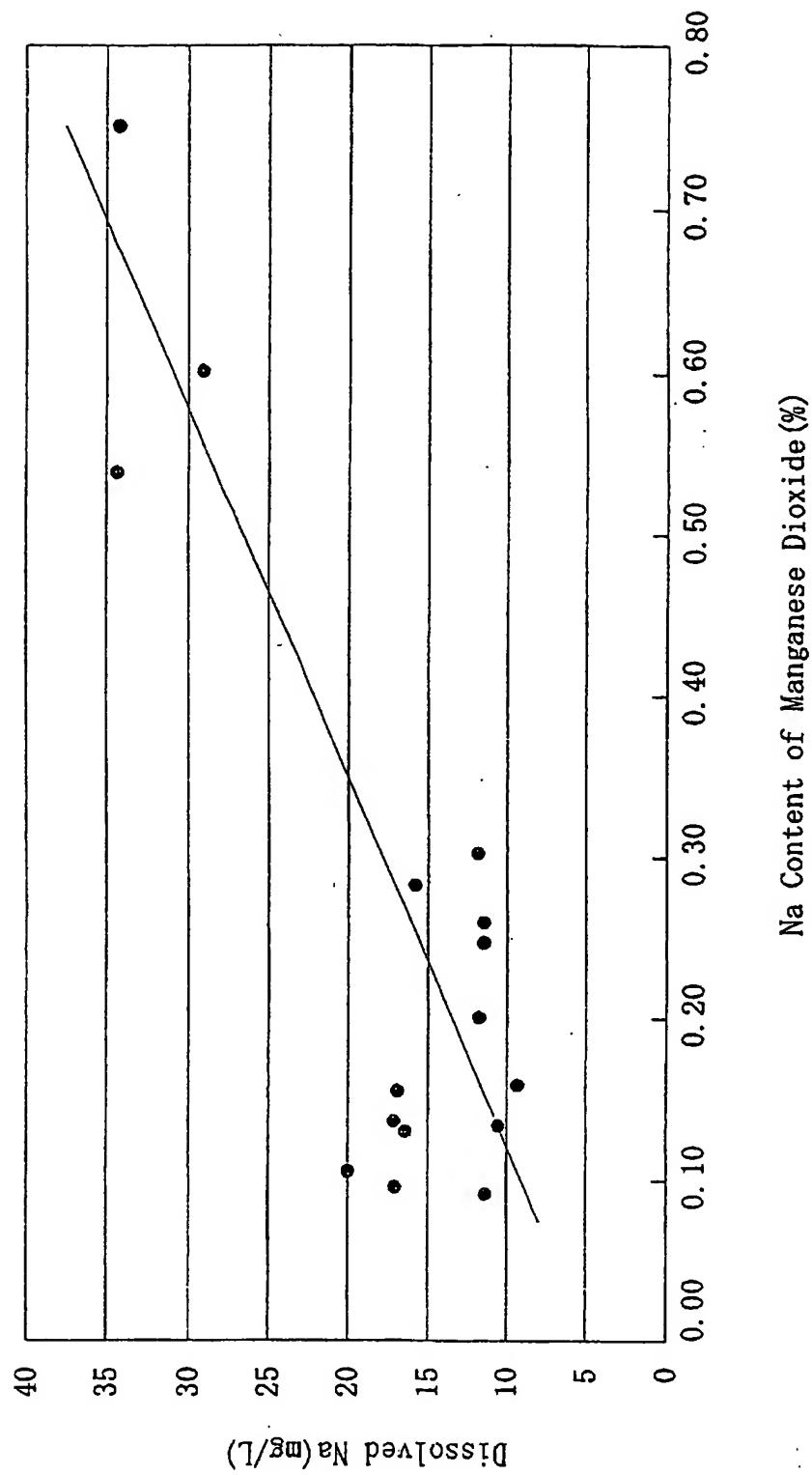


Fig. 4

